PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

pplicant's or agent's file reference 2011PC2-RTK	**FOR FURTHER ACTION**	See Form PCT/IPEA/416
ıternational application No. 'CT/AU2004/000428	International filing date *(day/month/year)* 2 April 2004	Priority date *(day/month/year)* 4 April 2003

ıternational Patent Classification (IPC) or national classification and IPC

nt. Cl. [7] C01B 39/02, 39/46

ıpplicant

NANOCHEM HOLDINGS PTY LTD et al

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. [X] *(sent to the applicant and to the International Bureau)* a total of **8** sheets, as follows:
      - [X] sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      - [ ] sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.

   b. [ ] *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or table related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).
4. This report contains indications relating to the following items:

[X]	Box No. I	Basis of the report
[ ]	Box No. II	Priority
[ ]	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
[X]	Box No. IV	Lack of unity of invention
[X]	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
[ ]	Box No. VI	Certain documents cited
[ ]	Box No. VII	Certain defects in the international application
[X]	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of the report
3 November 2004	11 July 2005
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer **N.L. KING** Telephone No. (02) 6283 2150

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/AU2004/000428

ox No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:

☐ international search (under Rules 12.3 and 23.1 (b))

☐ publication of the international application (under Rule 12.4)

☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

☐ the international application as originally filed/furnished

☒ the description:

pages **1-3, 5-52** as originally filed/furnished
pages* received by this Authority on with the letter of
page* **4** received by this Authority on **10 February 2005** with the letter of **10 February 2005**

☒ the claims:

pages as originally filed/furnished
pages* as amended (together with any statement) under Article 19
pages* received by this Authority on with the letter of
pages* **53-59** received by this Authority on **10 February 2005** with the letter of **10 February 2005**

☒ the drawings:

pages **1-12** as originally filed/furnished
pages* received by this Authority on with the letter of
pages* received by this Authority on with the letter of

☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages
☐ the claims, Nos.
☐ the drawings, sheets/figs
☐ the sequence listing (*specify*):
☐ any table(s) related to the sequence listing (*specify*):

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

☐ the description, pages
☐ the claims, Nos.
☐ the drawings, sheets/figs
☐ the sequence listing (*specify*):
☐ any table(s) related to the sequence listing (*specify*):

* *If item 4 applies, some or all of those sheets may be marked "superseded."*

ox No. IV Lack of unity of invention

☐ In response to the invitation to restrict or pay additional fees the applicant has:

☐ restricted the claims.

☐ paid additional fees.

☐ paid additional fees under protest.

☐ neither restricted nor paid additional fees.

☒ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is:

☐ complied with.

☒ not complied with for the following reasons:

Claims 1-26 relate to methods for making zeolite N whereas claims 29-61 relate to zeolite N of particular formulae.
The processes defined in claims 1-26 do not necessarily produce zeolites of the formulae defined in claims 29-61.
The zeolites defined in claims 29-61 are not necessarily produced by the processes defined in claims 1-26.
Consequently, these two sets of claims relate to different inventions.

4. Consequently, this report has been established in respect of the following parts of the international application:

☒ all parts.

☐ the parts relating to claims Nos.

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY	International application No. PCT/AU2004/000428

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Statement

Novelty (N)	Claims **1-61**	**YES**
	Claims	**NO**
Inventive step (IS)	Claims **1-61**	**YES**
	Claims	**NO**
Industrial applicability (IA)	Claims **1-61**	**YES**
	Claims	**NO**

Citations and explanations (Rule 70.7)

D1 Christensen, et al., "Crystal Structure Determination of Zeolite N from Synchrotron X-Ray Powder Diffraction Data", ACTA CHEMICA SCANDINAVICA, Vol.51 (1997), pages 969-973.

D2 Christensen, et al., "Neutron Powder Diffraction Study of the Dehydration of Zeolite N", ACTA CHEMICA SCANDINAVICA, Vol.53 (1999), pages 85-89.

D3 GB 1039345
D4 US 3306922
D5 US 3414602
D6 US 2996358
D7 US 4091079
D8 US 6218329

NOVELTY(N) Claims 1-61

Claim 1 defines a process for making zeolite N, the process comprising the steps of :-
(a) combining a water-soluble monovalent cation, hydroxyl anions and an aluminosilicate at a pH > 10, the molar ratio of water to Al_2O_3 being in the range 30 to 220, and

(b) heating and stirring the mixture to a temperature between 50°C and the boiling point until crystalline zeolite N is formed.

Claims 29-61 define zeolite N of particular formulae, and/or with particular physical properties and/or when used for particular purposes.

Related art appears in each of the above citations. However, none of the documents discloses a process as defined above for making zeolite N, or zeolite N having a composition and properties and uses as defined in the claims. Consequently, the claimed invention is novel.

INVENTIVE STEP(IS) Claims 1-61

The claimed invention involves an inventive step because it would not be obvious to a person skilled in the art to prepare and use zeolite N in accordance with the processes and formulae claimed.

ox No. VIII Certain observations on the international application

ıe following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully pported by the description, are made:

laim 1 is not clear in that the pressure applied while heating is not specified and hence the term "boiling point" is meaningless. Resolution of this matter is important because similar processes in the prior art are carried out at an elevated pressure whereas the present invention may be performed at "ambient pressures" (page 8 lines 15-17).

laims 29-61 are not supported by the description because the zeolites claimed are not necessarily prepared by the rocess of the invention. The process is an essential feature because, according to page 1 lines 6-8, the physical and hemical characteristics of the products are attributable to the method of production and according to page 5 lines 6-37, roperties (c), (d) and (f) are possessed only by zeolites prepared by the disclosed process.

Surprisingly, zeolites of N structure are formed at low temperature (less than 100°C) and without use of potassium chloride as an essential starting reactant as taught in the prior art. Contrary to prior art, zeolite N may be formed in the presence of caustic solutions such as KOH or NaOH although alkali halides such as NaCl may also be present.

The disclosed process enables the production of many varieties of zeolite with the N structure. In general, the compositions of zeolite N achievable by the synthesis process can be described by the formula:

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium (*e.g.* K, Na, NH_4); P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium ion, X = Cl or other halide and Y = OH, halide or other anion;

for $0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$.

Therefore the above formula equates to the term "zeolite N structure" as used herein.

As exemplified below, the method of the invention may give rise to potassium-only, potassium and sodium, potassium and ammonium and potassic high silica forms of zeolite N. Surprisingly, other forms of zeolite N produced by the disclosed invention include a potassium-only form with hydroxyl ion as the anion rather than chloride. These compositional variants have common properties arising from the method of production as described below. Other compositional variations to the forms described below are possible as will be appreciated by those skilled in the art.

Zeolites of this invention display a characteristically high proportion of external surface area (with values greater than $5m^2/g$), a distinctive X-ray diffraction pattern as shown in Figures 2, 5 and 6 and a high selectivity to ammonium and certain metal ions in the presence of alkali metal and alkaline earth ions in solution. In a powder X-ray diffraction pattern, the product of this process to make zeolite N shows a high background between the region $25° < 2\theta < 35°$. This high background intensity which ranges between 5% and 15% of the maximum peak height, may extend beyond $2\theta = 35°$ up to $2\theta = 70°$. This high background intensity is not observed in prior art on hydro-thermally synthesised zeolite N and suggests the presence of nano-sized crystals and/or amorphous aluminosilicate in association with zeolite N.

Without wishing to be bound by theory, the attributes of zeolite N formed by the process of this invention and the proximity of amorphous aluminosilicates (as described in US 6,218,329

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for making aluminosilicates of zeolite N structure comprising the steps of:
   (i) combining a water soluble monovalent cation, a solution of hydroxyl anions and an aluminosilicate to form a resultant mixture having a pH greater than 10 and a H_2O/Al_2O_3 molar ratio in the range 30 to 220;
   (ii) heating and stirring the resultant mixture to a temperature of between 50°C and the boiling point of the mixture for a time between 1 minute and 100 hours until a crystalline product of zeolite N structure is formed as determined by X-ray diffraction or other suitable characteristic; and
   (iii) separating the zeolite N product as a solid from the mixture.
2. A process as claimed in claim 1 wherein the water soluble monovalent cation in step (i) is an alkali metal or an ammonium ion or mixtures of these ions.
3. A process as claimed in claim 2 wherein the alkali metal comprises a potassium ion.
4. A process as claimed in claim 2 wherein the alkali metal comprises both a potassium and sodium ion.
5. A process as claimed in claim 2 wherein the monovalent cation comprises both potassium and ammonium ions.
6. A process as claimed in any preceding claim wherein the resultant mixture of step (i) also contains a halide.
7. A process as claimed in claim 6 wherein the halide is chloride.
8. A process as claimed in any preceding claim wherein the pH of the solution of hydroxyl ions is greater than 13.
9. A process as claimed in any preceding claim wherein in step (ii) the resultant mixture is heated to a temperature of in the range 80°C to 95°C.
10. A process as claimed in any preceding claim wherein the aluminosilicate has a Si:Al ratio in the range 1.0 to 5.0.
11. A process as claimed in claim 10 wherein the aluminosilicate has a Si:Al ratio in the range 1.0 to 3.0.
12. A process as claimed in claim 10 wherein the aluminosilicate is a clay.
13. A process as claimed in claim 12 wherein the clay is kaolin, meta-kaolin or montmorillonite or mixtures thereof.
14. A process as claimed in any preceding claim wherein in step (ii) said heating is carried out for a time in the range 2 to 24 hours.
15. A process as claimed in any preceding claim wherein the molar ratio of H_2O/Al_2O_3 in the mixture of step (i) is in the range 45 to 65.
16. A process as claimed in any preceding claim wherein in step (i) a quantity of solid zeolite N is added to the mixture.
17. A process as claimed in any preceding claim wherein caustic liquor remaining in the

mixture after step (iii) is re-used as at least part of a solution of anions and cations in step (i) for subsequent production of additional zeolite N product.

18. A process as claimed in claim 3 wherein the amount of potassium utilised is governed by a molar ratio of K_2O/Al_2O_3 in the range 0.3 to 15.

19. A process as claimed in claim 3 wherein the amount of potassium utilised is governed by a molar ratio of KCl/Al_2O_3 in the range 0.0 to 15.

20. A process as claimed in claim 7 wherein the amount of chloride utilised is governed by a molar ratio of KCl/Al_2O_3 in the range 0.0 to 15.

21. A process as claimed in claim 2 wherein the alkali metal is sodium and the amount of sodium utilised is governed by a molar ratio of Na_2O / Al_2O_3 in the range 0.0 to 2.5.

22. A process as claimed in claim 2 wherein the alkali metal is sodium and the amount of sodium utilised is governed by a molar ratio of NaCl / Al_2O_3 in the range 0.0 to 2.8.

23. A process as claimed in claim 7 wherein the amount of chloride utilised is governed by a molar ratio of NaCl / Al_2O_3 in the range 0.0 to 2.8.

24. A process as claimed in claim 7 wherein the amount of chloride utilised is governed by a molar ratio of Cl / SiO_2 in the range 0.0 to 6.5.

25. A process as claimed in claim 4 wherein the amount of sodium and potassium utilised is governed by a ratio of K/(K+Na) in the range 0.5 to 1.0.

26. A process as claimed in claim 4 wherein the amount of sodium and potassium utilised is governed by a ratio of (K + Na – Al)/ Si in the range 2.0 to 18.0.

27. Zeolite N produced by the process of any preceding claim or combination of preceding claims.

28. Zeolite N produced by the process of any preceding claim having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2$ nH_2O where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cation(s) exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$.

29. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2$ nH_2O where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

characterised in having a BET surface area greater than 1 m^2/g.

30. Zeolite N as claimed in claim 29 having a BET surface area between 1 m^2/g and 150 m^2/g.

31. Zeolite N as claimed in claim 30 having a BET surface area between 5 m^2/g and 150 m^2/g.

32. Zeolite N as claimed in any one of claims 29, 30 or 31 having a proportion of external surface area to internal surface area of greater than 1%.

33. Zeolite N as claimed in claim 32 having a proportion of external surface area to internal surface area of greater than 5%.

34. Zeolite N as claimed in claim 33 having a proportion of external surface area to internal surface area of greater than 10%.

35. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$
characterised in having an X-ray diffraction pattern which has a high background intensity of greater than 5% of a maximum peak height between the region $25° < 2\theta < 70°$.

36. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$
when used for exchange of ammonium ions in solution.

37. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$.
when used for exchange of ammonium ions in the presence of alkali metal and/or alkaline earth metal ions in solution.

38. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$.
having a cation exchange capacity ranging from 100 meq per 100g to 700 meq per 100g for ammonium ions with concentrations between less than 1 mg/L to greater than 10,000 mg/L.

39. Zeolite N as claimed in claim 38 having a cation exchange capacity greater than 200 meq per 100g.

40. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$
when used for exchange of metal ions in solution.

41. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$
when used for exchange of metal ions in the presence of alkali metal or alkaline earth metal ions in solution.

42. Zeolite N as claimed in claim 40 or 41 wherein the metal ions comprise copper, zinc, nickel, cobalt, cadmium, silver and lead.

43. Zeolite N as claimed in claim 40, 41 or 42 having cation exchange capacity for metal ions ranging from 20meq per 100g to 400meq per 100g.

44. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

when used for adsorbing ammonia gas in the temperature range 0°C to 300°C.

45. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

when used for adsorbing ammonia gas in the temperature range 0°C to 300°C in the presence of water.

46. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

when used for absorbing oil.

47. Zeolite N as claimed in claim 46 when used for absorbing oil greater than 50g of oil per 100g of Zeolite N.

48. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

when used for removing anions from wastewater.

49. Zeolite N having a composition according to the formula

$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where

M = alkali metal or ammonium;

P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium

X = halide and Y is an anion and

$0 \leq a \leq 1$, $1 \leq c/b \leq \infty$, $0 \leq d \leq 1$ and $1 \leq n \leq 10$

when used in an ammonium form to have a capacity to re-exchange alkali metal ions from solutions containing hydroxyl ions ranging in concentration from 0.1 M to

2.0M.

50. Zeolite N as claimed in claim 49 wherein the concentration of hydroxyl ions is from 0.4 M to 1.5 M.

51. Zeolite N as claimed in claim 49 or 50 wherein the solutions containing hydroxyl ions comprise KOH or NaOH or mixtures thereof.

52. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$
having a removal rate of ammonium ion ranging between 50-100% from ammonium loaded Zeolite N using a regeneration solution containing hydroxyl ions.

53. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$
when used to re-exchange ammonium ions and/or to retain high selectivity for ammonium ions after regeneration with a solution containing hydroxyl ions.

54. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$
when used to kill gram positive or gram negative bacteria.

55. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = potassium or sodium or ammonium;
P = silver or zinc
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$
when used to kill gram positive or gram negative bacteria.

56. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = potassium and ammonium;
P = silver and zinc
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$
when used to kill gram positive or gram negative bacteria.

57. Zeolite N having a composition according to the formula
$(M_{1-a}, P_a)_{12}(Al_bSi_c)_{10}O_{40}(X_{1-d}, Y_d)_2\ nH_2O$ where
M = alkali metal or ammonium;
P = alkali metal, ammonium or metal cations exchanged in lieu of alkali metal or ammonium
X = halide and Y is an anion and
$0 \leq a \leq 1,\ 1 \leq c/b \leq \infty,\ 0 \leq d \leq 1$ and $1 \leq n \leq 10$.
where c/b is greater than 1.

58. Zeolite N as claimed in claim 57 wherein c/b has an upper value of 5.

59. Zeolite N as claimed in claim 57 wherein c/b has an upper value of 3.

60. Zeolite N as claimed in any one of claims 28-59 wherein Y is hydroxyl or halide.

61. Zeolite N as claimed in claim 60 wherein Y is chloride.